# Polarographic Data and Deviations from Coplanarity of Helicene Molecules

By W. H. Laarhoven * and G. J. M. Brus, Department of Organic Chemistry, R.C. University, Nijmegen, The Netherlands

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION B
Physical Organic Chemistry

1971

# Polarographic Data and Deviations from Coplanarity of Helicene Molecules

By W. H. Laarhoven * and G. J. M. Brus, Department of Organic Chemistry, R.C. University, Nijmegen, The Netherlands

Values of polarographic half-wave potentials for eight helicenes indicate that the molecules of the compounds examined deviate from coplanarity to a similar extent.

In connection with investigations [1] into the photocyclization of diarylethylenes to helicenes it was important to know whether deviations from coplanarity in the overcrowded aromatic compounds synthesized were of a comparable degree.

From earlier polarographic studies [2] on planar aromatic compounds it is known that there is a linear relation between the half-wave potentials ($\varepsilon_{\frac{1}{2}}$) and the electron affinities, calculated by the Hückel MO-method.

Hoytink [3] found that sterically hindered molecules like binaphthyl have $\varepsilon_{\frac{1}{2}}$-values which are intermediate between those expected for the planar and the perpendicular conformation.

In a series of helicenes an increase in the deviation from coplanarity might, therefore, be accompanied by increasing deviations of the $\varepsilon_{\frac{1}{2}}$-values from the linear relation mentioned for planar aromatic compounds.

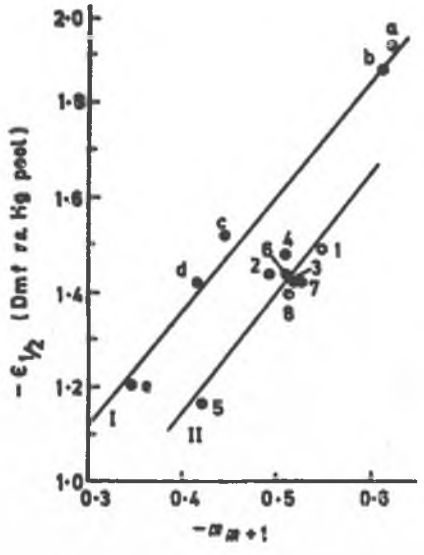
Half-wave potentials were measured in $10^{-3}$M deoxygenated dimethylformamide solutions with 0·1 mol $l^{-1}$ of tetra-n-butyl iodide as a supporting electrolyte. To check the apparatus and experimental conditions some planar aromatic compounds were also measured; the data are in good agreement with those given by Streitwieser [4] (line I in the Figure). The energies ($-m_{m+1}$) calculated for the lowest vacant molecular orbitals and the half-wave potentials, measured for several helicenes, are given in the Table and plotted in the Figure (line II). All half-wave potentials correspond to one-electron reductions. The experimental error of $\varepsilon_{\frac{1}{2}}$ was less than 0·02 V. Line II calculated by means of the method of least squares can be equated as follows

$$\varepsilon_{\frac{1}{2}} = 2{\cdot}48\, m_{m+1} - 0{\cdot}16 \quad (r = 0{\cdot}930)$$

The equation of curve I as given by Streitwieser [4] is

$$\varepsilon_{\frac{1}{2}} = 2{\cdot}407\ (\pm 0{\cdot}182)\, m_{m+1} - 0{\cdot}396\ (\pm 0{\cdot}093)$$

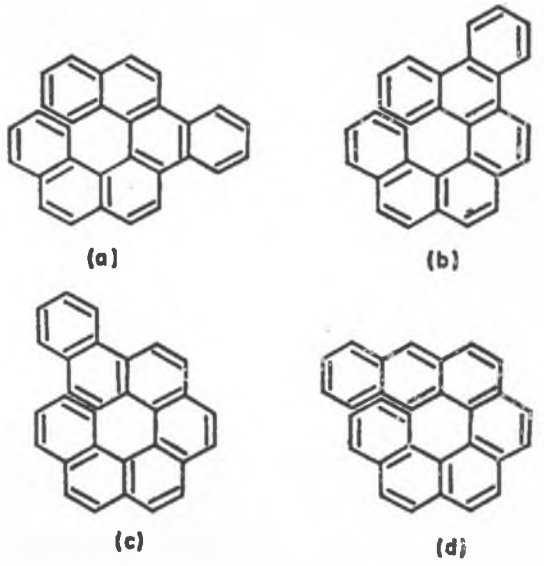
It is evident that the slope of both lines is similar. Consequently, all helicenes investigated deviate to an




Polarographic half-wave potential *vs.* electron affinity: a = naphthalene, b = phenanthrene, c = pyrene, d = anthracene, and e = perylene; 1 = hexahelicene, 2 = benzo[*d*]hexahelicene, 3 = benzo[*a*]hexahelicene, 4 = benzo[*m*]hexahelicene, 5 = benzo[*n*]hexahelicene, 6 = heptahelicene, 7 = octahelicene, 8 = nonahelicene, and Dmf = dimethylformamide

HMO electron affinities ($-m_{m+1}$) and half-wave potentials ($-\varepsilon_{\frac{1}{2}}$) of helicenes

| | $-m_{m+1}$ ($\beta$-units) | $-\varepsilon_{\frac{1}{2}}$ (V) |
|---|---|---|
| (1) Hexahelicene | 0·546 | 1·49 |
| (2) Benzo[*d*]hexahelicene (a) | 0·493 | 1·44 |
| (3) Benzo[*a*]hexahelicene (b) | 0·517 | 1·43 |
| (4) Benzo[*m*]hexahelicene (c) | 0·510 | 1·48 |
| (5) Benzo[*n*]hexahelicene (d) | 0·418 | 1·17 |
| (6) Heptahelicene | 0·511 | 1·44 |
| (7) Octahelicene | 0·523 | 1·43 |
| (8) Nonahelicene | 0·513 | 1·40 |




[1] W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron*, 1970, **26**, 4865.

[2] See for a review: A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' John Wiley, New York, London, 1961, p. 175.

[3] G. J. Hoytink, *Rec. Trav. chim.*, 1955, **74**, 1525.

[4] A. Streitwieser, jun., and I. Schwagir, *J. Phys. Chem.*, 1962, **66**, 2316.

equal degree from the line for planar aromatic compounds. The deviation can be explained by two factors. (1) The calculation of the lowest vacant MO concerns helicenes in a hypothetic planar conformation; this causes a shift of line II in a horizontal direction. (2) It is unlikely that differences in entropy and solvation energy for molecules and their anions in a series of helicenes and in planar aromatics are equal; this results in a shift in a vertical direction.

Probably the second factor is the more important. It is known [5] that several planar aromatic compounds like triphenylene, coronene, and decacyclene also fail to fit Streitwieser's line I.

Moreover, we found that a plot of the frequencies of the charge-transfer absorption band ($\nu_{max.}$) of the helicenes with tetracyanobenzoquinodimethane as an acceptor against the energy of the highest occupied MO of the helicenes shows only a small deviation from a similar plot found for planar aromatic compounds. It must be stated, however, that the latter argument is not very strong, because as the band width of the charge transfer absorptions of helicenes is very large, $\nu_{max.}$ cannot be determined very accurately, which causes low correlation coefficients of the relative plot.

[5] G. J. Hoytink, personal communication.
[6] R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *Tetrahedron Letters*, 1968, 3507.

## EXPERIMENTAL

The substances used for checking the experimental conditions were of analytical quality.

The helicenes were synthesized by photocyclizations of the appropriate diarylethylenes.[1,6] (1) Hexahelicene, m.p. 231°; (2) benzo[*d*]hexahelicene, m.p. 212—214°; (3) benzo[*a*]-hexahelicene, m.p. 250—253°; (4) benzo[*m*]hexahelicene, m.p. 252—253°; (5) benzo[*n*]hexahelicene, m.p. 275—277°; (6) heptahelicene, m.p. 253—254°; (7) octahelicene, m.p. 331°; (8) nonahelicene, m.p. 358—360°.

The dimethylformamide used was fractionated under oxygen-free nitrogen. The fraction boiling at 154—155° was used. All handling of the solvent or solutions, including the polarographic reductions, was carried out under nitrogen.

The polarographic analyses were carried out with a Metrohm Polarecord E 261 with I.R. compensator E 446 and a three-electrode geometry. A dropping-mercury electrode was used as a cathode, a Hg pool anode as reference, and a Pt wire as a work electrode. All $\varepsilon_{\frac{1}{2}}$ values were measured *vs.* Hg pool. Differences between two independent measurements of the same compound were in all cases less than 0·02. Plotting $E$ against $\log [i/(id - i)]$ gave a straight line with a slope in the range of 0·052—0·069 indicating a reversible one electron reduction.

The electron affinities were calculated by the simple Hückel MO-method assuming planar structures. The calculations were carried out with an IBM 360—50 computer.

[0/2132 *Received*, *November 26th*, 1970]